

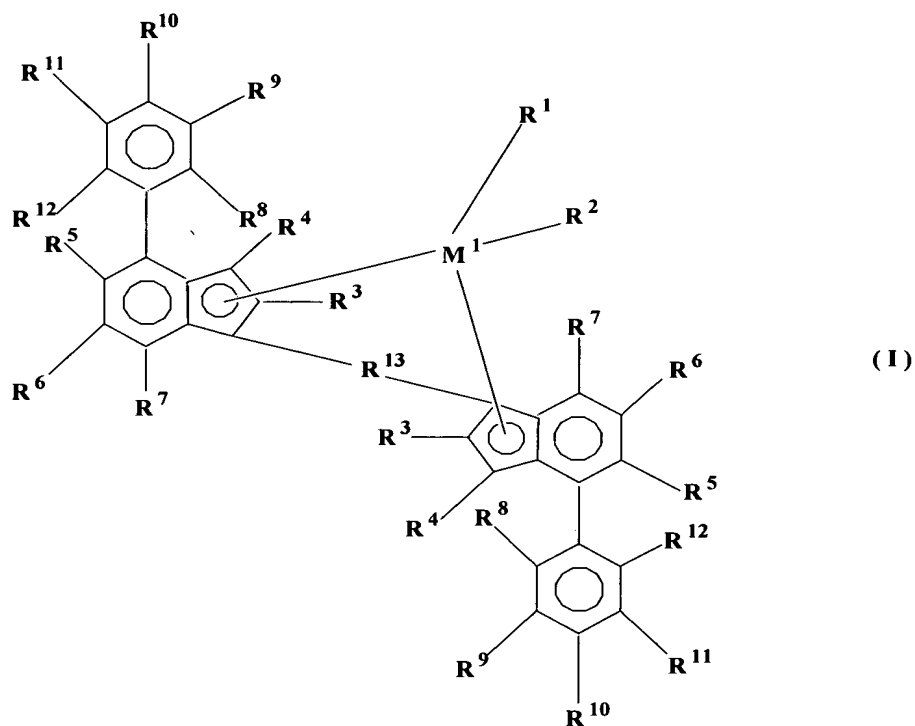
CLAIMS

WHAT IS CLAIMED IS:

1. A process of preparing a copolymer composition that includes a diene-modified propylene random copolymer, comprising:
 - contacting a metallocene catalyst compound with a polymerization medium that includes at least a propylene monomer and an α , internal non-conjugated diene monomer; and
 - conducting polymerization of the monomers in the presence of the metallocene catalyst compound for a time sufficient to provide a diene-modified polypropylene random copolymer that includes monomeric units derived from each of the monomers, and having from 0.0 wt% to 2.0 wt% ethylene and a heat of fusion of 30 J/g or more.
2. A process of preparing a polymer composition that includes a diene-modified propylene random copolymer, comprising:
 - contacting a metallocene catalyst compound having at least two indenyl rings or derivatives of indenyl rings, each ring being substituted at the 2 and/or 4 positions, with a polymerization medium that includes at least a propylene monomer and an α , internal non-conjugated diene monomer that has an internal double bond comprising a di-substituted vinyl group or a tri-substituted vinyl group; and
 - conducting polymerization of the monomers in the presence of the metallocene catalyst compound for a time sufficient to provide a diene-modified polypropylene random copolymer that includes monomeric units derived from each of the monomers, and having from 0.0 wt% to 2.0 wt% ethylene and a heat of fusion of 30 J/g or more.
3. The process of claim 1, in which the α , internal non-conjugated diene monomer has an internal double bond comprising a di-substituted vinyl group or a tri-substituted vinyl group.

4. The process of claim 1, in which the α , internal non-conjugated diene monomer has an internal double bond comprising a di-substituted vinyl group or a tri-substituted vinyl group having one or more methyl group substituents.
5. The process of claim 1, on which the α , internal non-conjugated diene monomer has an internal double bond comprising a tri-substituted vinyl group having two methyl group substituents.
6. The process of claim 1, in which the α , internal non-conjugated diene monomer comprises 2-methyl-1,5-hexadiene or 7-methyl-1,6-octadiene.
7. The process of claim 1, in which the metallocene catalyst compound is or includes a substituted or unsubstituted silyl-bridged or ethylene-bridged bis-indenyl metallocene.
8. The process of claim 1, in which the metallocene catalyst compound comprises a bridged metallocene compound having at least two indenyl rings or derivatives of indenyl rings, each ring being substituted at the 2 position.
9. The process of claim 1, in which the metallocene catalyst compound comprises a bridged metallocene compound having at least two indenyl rings or derivatives of indenyl rings, each ring being substituted at the 2 and 4 positions.
10. The process of claim 1, in which the metallocene catalyst compound comprises supported dimethylsilylbis (2-methyl-4-phenyl-1-indenyl) zirconium dimethyl.

11. The process of claim 1, in which the metallocene catalyst compound is activated with a dimethylanilinium tetrakis (perfluorophyl) boron activator.
12. The process of claim 1, in which the metallocene catalyst compound is activated with a methlyaluminoxane activator.
13. The process of claim 1, in which the metallocene catalyst compound is represented by the formula:



wherein:

M^1 is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten;

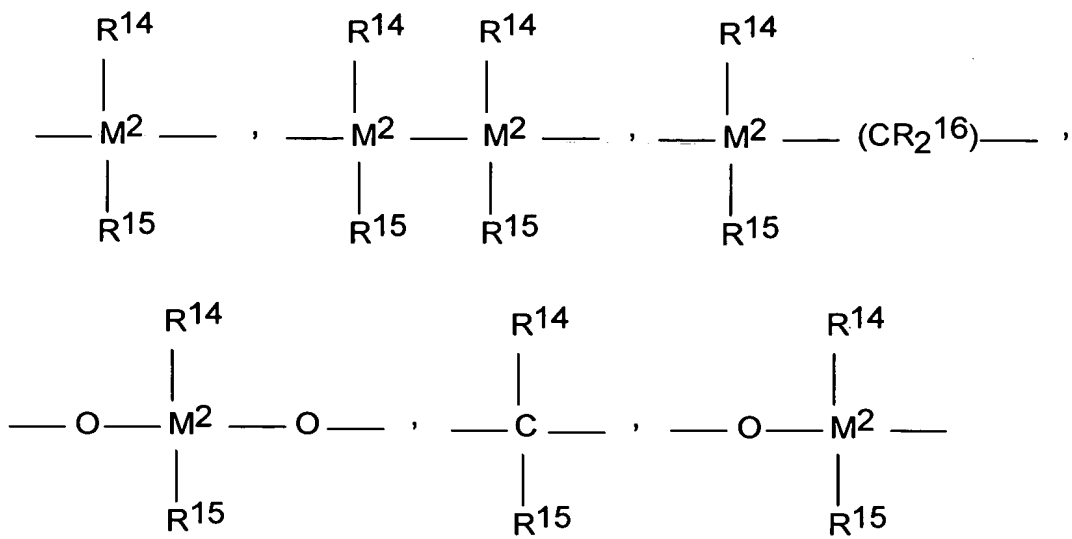
R^1 and R^2 are identical or different, and are one of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_2 - C_{40} alkenyl group, a C_7 -

C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, an OH group or a halogen atom; R¹ and R² may also be joined together to form an alkanediyl group or a conjugated C₄₋₄₀ diene ligand which is coordinated to M¹ in a metallocyclopentene fashion; R¹ and R² may also be identical or different conjugated dienes, optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl)silyl groups or hydrocarbyl, tri(hydrocarbyl)silylhydrocarbyl groups, said dienes having up to 30 atoms not counting hydrogen and forming a π complex with M, examples include 1,4-diphenyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,4-hexadiene, 1-phenyl-1,3-pentadiene, 1,4-dibenzyl-1,3-butadiene, 1,4-ditolyl-1,3-butadiene, 1,4-bis(trimethylsilyl)-1,3-butadiene, and 1,4-dinaphthyl-1,3-butadiene;

Each R³ is identical or different from the other R³ and is each a hydrogen atom, a halogen atom, a C₁-C₁₀ alkyl group which may be halogenated, a C₆-C₁₀ aryl group which may be halogenated, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ -arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, a -NR'₂, -SR', -OR', -OSiR'₃ or -PR'₂ radical, wherein R' is one of a halogen atom, a C₁-C₁₀ alkyl group, or a C₆-C₁₀ aryl group;

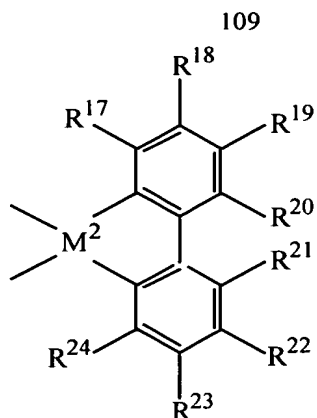
R⁴ to R⁷ are identical or different and are hydrogen, or are as defined for R³ or two or more adjacent radicals R⁵ to R⁷ together with the atoms connecting them form one or more rings;

R¹³ is



-B(R¹⁴)-, -Al(R¹⁴)-, -Ge-, -Sn-, -O-, -S-, -SO-, -SO₂-, -N(R¹⁴)-, -CO-, -P(R¹⁴)-, or -P(O)(R¹⁴)-;

wherein: R¹⁴, R¹⁵ and R¹⁶ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ branched or linear alkyl group, a C₁-C₂₀ fluoroalkyl or silaalkyl group, a C₆-C₃₀ aryl group, a C₆-C₃₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, a C₂-C₂₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, a C₇-C₄₀ alkylaryl group, or R¹⁴ and R¹⁵, together with the atoms binding them, form a cyclic ring; or, R¹³ is represented by the formula:

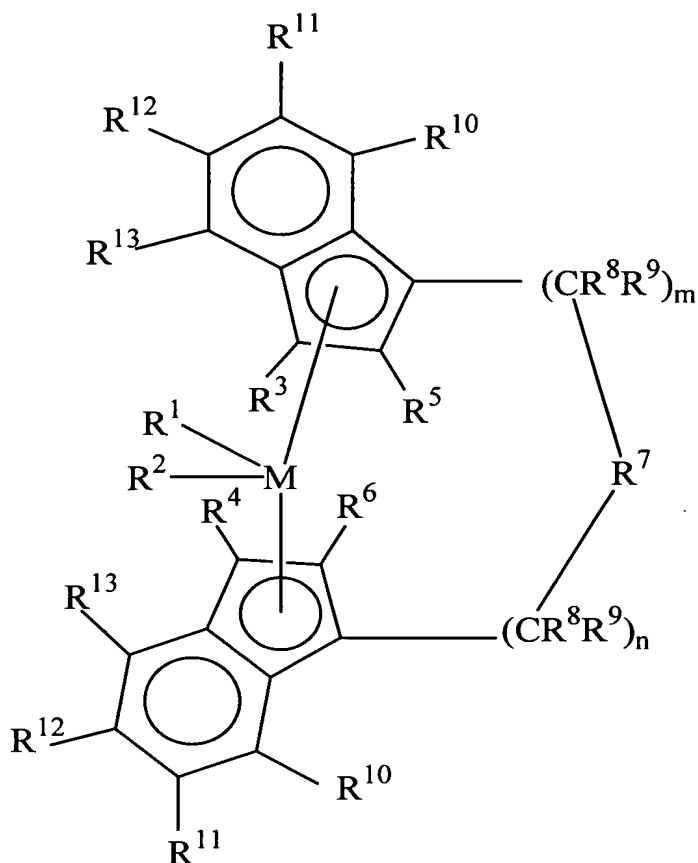


wherein: R^{17} to R^{24} are as defined for R^1 and R^2 , or two or more adjacent radicals R^{17} to R^{24} , including R^{20} and R^{21} , together with the atoms connecting them form one or more rings;

M^2 is one or more carbons, silicon, germanium or tin; and

R^8 , R^9 , R^{10} , R^{11} and R^{12} are identical or different and have the meanings stated for R^4 to R^7 .

14. The process of claim 1, in which the metallocene catalyst compound is represented by the formula:



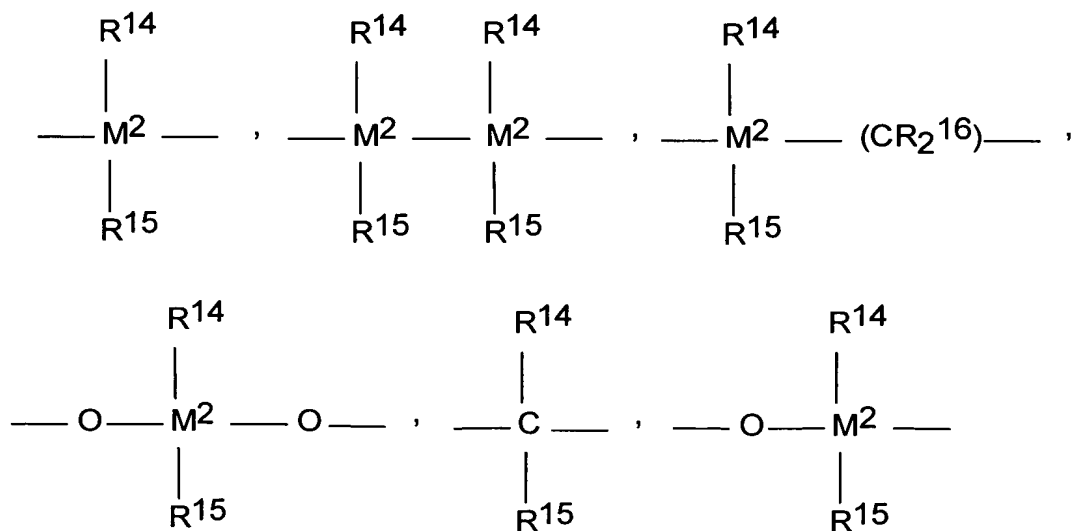
wherein: M is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium and hafnium;

R^1 and R^2 are identical or different, and are one of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, or a halogen atom, or a conjugated diene which is optionally substituted with one or more hydrocarbyl, tri(hydrocarbyl)silyl groups or hydrocarbyl, tri(hydrocarbyl)silylhydrocarbyl groups, said diene having up to 30 atoms not counting hydrogen;

R^3 and R^4 are defined the same as are R^1 and R^2 ;

R^5 and R^6 are identical or different, and are one of a hydrogen atom, a halogen atom, a C_1 - C_{10} alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein: R^{15} is one of a halogen atom, a C_1 - C_{10} alkyl group, or a C_6 - C_{10} aryl group;

R^7 is



$-B(R^{14})-$, $-Al(R^{14})-$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-N(R^{14})-$, $-CO-$, $-P(R^{14})-$, or $-P(O)(R^{14})-$;

wherein: R^{14} , R^{15} and R^{16} are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{20} branched or linear alkyl group, a C_1 - C_{20} fluoroalkyl or silaalkyl group, a C_6 - C_{30} aryl group, a C_6 - C_{30} fluoroaryl group, a C_1 - C_{20} alkoxy group, a C_2 - C_{20} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_8 - C_{40} arylalkenyl group, a C_7 - C_{40} alkylaryl group, or R^{14} and R^{15} , together with the atoms binding them, form a cyclic ring;

M^2 is carbon, silicon, germanium or tin;

R^8 and R^9 are R^8 and R^9 , are identical or different, and have the meanings stated for R^5 and R^6 ;

R^{10} , R^{11} , R^{12} and R^{13} are identical or different and have the meanings stated for R^5 and R^6 ; wherein at least one of R^{13} and R^{10} are identical or different, and are one of a hydrogen atom, a halogen atom, a C_1 - C_{10} alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein: R^{15} is one of a halogen atom, a C_1 - C_{10} alkyl group, or a C_6 - C_{10} aryl group; and

m and n are identical or different and are zero, 1 or 2, m plus n is zero, 1.

15. The process of claim 1, in which the polymerization medium is substantially gel-free following formation of the polypropylene/diene copolymer.
16. The process of claim 1, further comprising crosslinking the polypropylene copolymer.
17. The process of claim 1, in which polymerization medium has less than 90 volume percent diluent.
18. The process of claim 1, in which polymerization medium has less than 50 volume percent diluent.
19. The process of claim 1, in which polymerization medium has less than 30 volume percent diluent.
20. The process of claim 1, in which the final polypropylene copolymer is isotactic or syndiotactic or atactic.

21. The process of claim 1, in which the metallocene catalyst compound is combined with the monomers in the absence of hydrogen or in the presence of hydrogen in an amount of up to 1.0 mole% hydrogen in the reactor.
22. The process of claim 1, in which the heat of fusion of the propylene copolymer is 25 J/g or more.
23. The process of claim 1, in which the heat of fusion of the propylene copolymer is 50 J/g or more.
24. The process of claim 1, in which the heat of fusion of the propylene copolymer is 70 J/g and 100 J/g or more.
25. The process of claim 1, in which the propylene copolymer has a Branching Index of 1.0 or less.
26. The process of claim 1, in which the propylene copolymer has a Branching Index of 0.95 or less.
27. The process of claim 1, in which the propylene copolymer has a Branching Index of 0.90 or less.
28. The process of claim 1, in which the propylene copolymer has a Branching Index of 0.80 or less.
29. A copolymer composition comprising a diene-modified polypropylene random copolymer having propylene units; diene units derived from α , internal non-conjugated diene monomers; from 0.0 wt% to 20 wt% ethylene units; and a heat fusion of 25 J/g or more.

30. The copolymer composition of claim 29 in which the diene units derived from α , internal non-conjugated diene monomers are present in the polypropylene copolymer in an amount of from 0.0005 mol% to 10 mol%.
31. The copolymer composition of claim 29 in which the diene units derived from α , internal non-conjugated diene monomers are present in the polypropylene copolymer in an amount of from 0.005 mol% to 1 mol%.
32. The copolymer composition of claim 29, in which the α , internal non-conjugated diene monomer is selected from the group consisting of 2-methyl-1,5-hexadiene and 7-methyl-1, 6-octadiene.
33. The polymer composition of claim 29, in which the propylene copolymer has a crystallization temperature (T_c) of 25 °C or more.
34. The polymer composition of claim 29, in which the propylene copolymer has a crystallization temperature (T_c) of 50 °C or more.
35. The polymer composition of claim 29, in which the propylene copolymer has a crystallization temperature (T_c) of 75 °C or more.
36. The polymer composition of claim 29, in which the propylene copolymer has a crystallization temperature (T_c) of 110 °C or more.
37. The polymer composition of claim 29, in which the propylene copolymer has a crystallization temperature (T_c) of from 25°C to 115 °C.
38. The polymer composition of claim 29, in which the propylene copolymer has a melting point (T_m) of 50 °C or more.
39. The polymer composition of claim 29, in which the propylene copolymer has a melting point (T_m) of 75 °C or more.

40. The polymer composition of claim 29, in which the propylene copolymer has a melting point (T_m) of 100 °C or more.
41. The polymer composition of claim 29, in which propylene copolymer has a melting point (T_m) of 125 °C or more.
42. The polymer composition of claim 29, in which the propylene copolymer has a melting point (T_m) of 165 °C or more.
43. The polymer composition of claim 29, in which the propylene copolymer has a melting point (T_m) of from 50 °C to 165°C.
44. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 0.01 or more.
45. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 0.1 or more.
46. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 0.5 or more.
47. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 0.7 or more.
48. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 1.0 or more.
49. The polymer composition of claim 29, in which the propylene copolymer has a melt flow rate of 1.5 or more.